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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a **PROVISIONAL APPLICATION FOR PATENT** under 37 CFR 1.53 (b)(2).

Docket Number	26392	Type a plus sign (+) inside this box ->	+

INVENTOR(s) / APPLICANT(s)

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TITLE OF THE INVENTION (280 characters max)

HYDROPHOBIC COMPOSITES AND METHODS OF MAKING SAME

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ENCLOSED APPLICATION PARTS *(check all that apply)*

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☐ Drawing(s)	*Number of Sheets*	X	☑ Other (specify) 58 Claims

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Respectfully submitted,

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☐ Additional inventors are being named on separately numbered sheets attached hereto

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

APPLICATION FOR PATENT

Inventor: Zeev Birger

Title: HYDROPHOBIC COMPOSITES AND METHODS OF MAKING SAME

FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to hydrophobic composites and methods of producing same. More particularly, the present invention relates to hydrophobic composites having a core material coated by a hydrophobic powder, the hydrophobic powder comprises an impure element pre-treated with a hydrophobic hydrocarbon, optionally the core material is co-coated also with additional coating agents, thereby providing hydrophobic composites with superior water-repellency and durability.

Hydrophobic coatings of aggregates and various other surfaces for waterproofing applications and for cleaning up oil spills have been known for over 35 years and are disclosed in a few disclosures. For example, a number of water-repellent composite materials composed of various absorbent substrates coated with organosilicon compositions have been proposed for use in removing oil or oil film from water contaminated therewith.

One such material is disclosed in U.S. Patent No. 3,562,153, to Tully et al. The oil absorbent compositions of the Tully et al. patent are obtained by treating a liquid absorbent material, which may be particulate, granular or fibrous in nature, with a colloidal metal or metalloid oxide which is chemically bonded to an organosilicon compound to render the metal or metalloid oxide hydrophobic. The hydrophobic oxide-treated absorbent composition is contacted with the oil-contaminated water and selectively removes the oil therefrom. The oil absorbent composition of Tully et al. is reported to have excellent water repellency, thus enabling it to maintain its oil absorbent efficiency for long immersion periods.

U.S. Patent No. 4,474,852, to Craig, which is incorporated by reference as if fully set forth herein, discloses that hydrophobic composites having superior water repellency are obtainable by depositing on a particulate and granular core material an adherent first coat which comprises a film-forming polyurethane and asphalt, as an optional additive, and applying to the thus coated core material a second coat

comprising a hydrophobic colloidal oxide such as, for example, hydrophobic fumed silica. According to the teachings of Craig, the adherent first coat should not exceed 1 weight percentage of the total dry aggregate weight while the second coat is between 0.025 and 0.25 weight percentage of this total weight. Further according to the teachings of Craig, hydrophobic composites prepared in this manner not only prevent water from adhering to the surfaces of the individual composite particles, but also from entering the interstitial spaces of the aggregates of the composites.

WO 03/044124, which is also incorporated by reference as if fully set forth herein, also discloses a method of preparing hydrophobic aggregates, which is based on the teachings of Craig (U.S. Patent No. 4,474,852). According to the teachings of WO 03/044124, the hydrophobic aggregates disclosed in U.S. Patent No. 4,474,852 are not satisfactory as they do not withstand water pressure higher than 2-3 centimeters.

In a search for a method of producing hydrophobic aggregates with improved water-repellency and oil absorbency performance and improved durability under higher water pressures, it was concluded, according to the teachings of WO 03/044124, that an improved method of preparing hydrophobic aggregates, as compared with the teachings of Craig, should include changes relating to the compositions of the first and second coat and the relative amounts thereof, to the temperature in the various process steps and to the mixing rate during the course of preparation.

Hence, the method disclosed in WO 03/044124 includes depositing on a core material an adherent first coat which comprises a film-forming agent such as polyurethane and optionally a gluing agent such as liquid asphalt, and applying to the thus coated core material a second coat which comprises a hydrophobic fumed silicate or any other superhydrophobic powder. According to the teachings of WO 03/044124, the adherent first coat constitutes about 1-2 weight percentages of the total dry aggregate weight while the second coat constitutes more than 5 weight percentages of this total weight. Further according to the teachings of WO 03/044124, such hydrophobic composites are capable of holding a water pressure of up to 20-30 cm.

Although WO 03/044124 teaches the use of superhydrophobic powders other than hydrophobic fumed silica, this reference neither specifies nor exemplifies such a

superhydrophobic powder. This reference also fails to demonstrate any performance of the hydrophobic composites disclosed therein with regard to both, water repellency and its behavior under high water pressures. Furthermore, it is well known in the art that using such a large amount of hydrophobic fumed silica as the second coat, as taught by WO 03/044124, reduces the cost-effectiveness as well as the simplicity of the process.

In addition, as hydrophobic fumed silica, as well as other metal oxides treated with organosilicon compounds, such as those disclosed in the Craig patent, are characterized as acidic substances, aggregates coated by such materials are susceptible to reactions with alkaline reagents such as detergents. This feature limits the use of such aggregates in applications where detergents may be in contact with the hydrophobic aggregates, such as, for example, top-coatings of various surfaces.

Hence, although the prior art teaches methods of producing hydrophobic composites, these presently known methods do not result in satisfactory products and are further limited by other parameters, such as, for example, cost effectiveness.

There is thus a widely recognized need for, and it would be highly advantageous to have hydrophobic composites and methods of making same devoid of the above limitations.

SUMMARY OF THE INVENTION

While conceiving the present invention, the inventor has envisioned that by further changing the constituents of the first and second coats and the relative amounts thereof, cost-efficient hydrophobic composites with improved physical and chemical performances would be obtainable. Particularly, it has been hypothesized that by using as a coat a hydrophobic powder comprised of impure elements that have been pre-treated with a hydrocarbon such as a long-chain fatty acid (e.g., stearic acid), hydrophobic composites with improved performance would be cost-efficiently obtainable.

While reducing the present invention to practice, it was indeed found that by using the hydrophobic powder described above, hydrophobic composites having superior physical and chemical performances as compared with the presently known hydrophobic composites were obtained. These newly disclosed composites comprise a hydrophobic coating which constitutes not more than 5 weight percentages of the total

weight of the composite and are characterized by superb water-repellency and other beneficial properties, as is detailed hereinbelow.

Thus, according to one aspect of the present invention there is provided a hydrophobic composite that comprises a core material coated by a hydrophobic powder. The hydrophobic powder comprises one or more impure element(s) having a hydrocarbon chain attached thereto.

According to further features in preferred embodiments of the invention described below, the hydrocarbon chain comprises at least 10 carbon atoms.

According to still further features in the described preferred embodiments the hydrocarbon chain is covalently attached to the impure element(s).

According to still further features in the described preferred embodiments the hydrocarbon is a residue of a fatty acid having at least 12 carbon atoms, such as, but not limited to, stearic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linolenic acid and arachidonic acid.

According to still further features in the described preferred embodiments the element can be a metallic element, a semi-metallic element or a transition metallic element, such as, but not limited to, magnesium, calcium, aluminum, zinc, sodium, barium, zirconium, manganese, titanium, vanadium, chromium, iron and combinations thereof.

According to still further features in the described preferred embodiments the hydrophobic powder has an average particle size ranging between 0.1 micron and 50 microns, and typically has a surface area ranging between 1 m^2/gram and 60 m^2/gram.

According to still further features in the described preferred embodiments the hydrophobic powder further comprises hydrophobic fumed silica, which constitutes between 1 and 99 weight percentages of the hydrophobic powder.

According to still further features in the described preferred embodiments the hydrophobic powder described above constitutes between about 0.1 and about 5 weight percentages of the hydrophobic composite.

According to further features in preferred embodiments of the invention described below, the core material is a particulate or granulate material, having an average particle size that ranges between 25 millimeters and 5 microns.

According to still further features in the described preferred embodiments the core material is selected from the group consisting of sand, gravel, slag, porcelanit,

dolomite, porcelain, basalt, quartz sand, coal ash, chalk, zeolite, montmorillonite, agapultite, flint, bentonite, perlite, mica, wood chips, nut shells, sawdust and combinations thereof.

According to further features in preferred embodiments of the invention described below, the hydrophobic powder is bonded to the core material via an adherent layer.

According to still further features in the described preferred embodiments the adherent layer comprises a film-forming agent, preferably a film forming polyurethane.

According to still further features in the described preferred embodiments the adherent layer further comprises a gluing agent, which is preferably a volatile hydrocarbon having at least 12 carbon atoms, such as, but not limited to, liquid asphalt, paraffin wax, beeswax, lanolin wax, linseed oil and combinations thereof. The gluing agent typically constitutes between about 0.1 and about 50 weight percentages of the adherent layer.

According to still further features in the described preferred embodiments the adherent layer constitutes between about 0.5 and about 7 weight percentages of the hydrophobic composite.

According to still further features in the described preferred embodiments the hydrophobic composite of the present invention further comprises at least one additive such as, but not limited to, a coloring agent, a UV resistant agent, a bleaching agent and an abrasive agent. The coloring agent preferably constitutes between about 0.1 and about 2 weight percentages of the hydrophobic composite. The UV resistant agent and the bleaching agent each preferably constitute between about 0.01 and about 2 weight percentages of the hydrophobic composite. The abrasive agent preferably constitutes between about 0.1 and about 0.5 weight percentages of the hydrophobic composite.

The hydrophobic composite described hereinabove are typically characterized as being inactive toward alkaline reagents.

The hydrophobic composite is further characterized as being capable of preventing water adherence thereto and water penetration therein under an external pressure of up to about 4.5 atmospheres, and as being durable to dynamic water wear for at least 2 months.

According to another aspect of the present invention, there is provided a method of preparing a hydrophobic composite, which comprises coating the core material described hereinabove with the hydrophobic powder described hereinabove, to thereby provide the hydrophobic composite.

According to further features in preferred embodiments of the invention described below, the method further comprises, prior to the coating, applying onto the core material the adherent layer described hereinabove. The applying of the adherent layer is preferably effected by admixing the core material with an adherent mixture containing a film-forming agent and a volatile solvent, while removing all of the volatile solvent from the resulting mixture, to thereby provide the core material having applied thereon the adherent layer. The volatile solvent is preferably an organic solvent having a boiling temperature ranging between about 80 °C and 200 °C. The removing of the solvent can be performed either by evaporative heating or at room temperature.

According to still further features in the described preferred embodiments the method further comprises drying the core material prior to coating it by the hydrophobic powder or to admixing it with the adherent layer mixture.

According to still further features in the described preferred embodiments the method further comprises, after the coating, curing the hydrophobic composite. The curing is preferably performed for a time period that ranges between 1 and 30 days.

According to still further features in the described preferred embodiments the method further comprises, prior to coating the core material, admixing the core material or the core material having thereon the adherent layer with an additive such as, but not limited to, a coloring agent, a UV resistant agent, a bleaching agent and an abrasive agent.

The present invention successfully addresses the shortcomings of the presently known configurations by providing a hydrophobic composite with superior chemical and physical properties and an efficient method of preparing such a hydrophobic composite.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable

methods and materials are described below. In case of conflict, the patent specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of novel hydrophobic composites that have superior chemical and physical performances, which can be beneficially used in various waterproofing and oil-absorbing applications, and of methods of their production. Specifically, the hydrophobic composites of the present invention comprise a core and coating compositions which render the resulting product durable toward a myriad of parameters encountered in water-proofing applications such as, for example, high water pressures, wear, reactive detergents and more. The hydrophobic composites of the present invention are manufacturable far cost effectively as compared to the prior art hydrophobic composites described in the background section above.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

As is discussed in the Background section hereinabove, the presently known hydrophobic composites are limited by both their performance and their effectiveness. For example, the hydrophobic composites disclosed by Craig, in U.S. Patent No. 4,474,852, were found incapable of withstanding water pressures higher than 2-3 cm and hence cannot be practically used in various common waterproofing applications, such as for example, as a coat of water reservoirs and as a gravel fill or ballast for road beds or sidewalks, where water-repellency under high pressures is required. The hydrophobic composites disclosed in WO 03/044124 include a hydrophobic coating that is consisted essentially of hydrophobic fumed silica, which is both highly expensive and render the composite's surface acidic and hence susceptible to reactive detergents. Such hydrophobic composites, apart from being economically inefficient, cannot be efficiently used in various applications such as topcoats of various surfaces.

In a search for hydrophobic composites with improved performances, the present inventor has found that hydrophobic composites that include as the hydrophobic coat a hydrophobic powder of one or more impure elements having one or more hydrocarbons attached thereto, optionally in combination with the commercially available hydrophobic fumed silica, can be prepared in an environmental-friendly and economically-efficient process and exert superior water-repellency as well as durability toward parameters such as high water pressures, dynamic water wear and reactive detergents.

Hence, according to one aspect of the present invention there is provided a hydrophobic composite which comprises a core material coated by a hydrophobic powder, the powder comprises one or more impure elements having a hydrocarbon chain attached thereto.

As used herein, the phrase "impure element" includes chemical elements of the periodic table which are not used in their pure form. The impure elements can be naturally impure elements such as, for example, oxidized elements or carbonated elements or can be pure or impure elements which have been further impurified by, for example, small quantities of other elements and/or various organic substances. The impurity of the element(s) is required so as to render the element susceptible to a surface reaction with an organic substance bearing the hydrocarbon chain, as is further detailed hereinbelow.

The selected elements are preferably metallic, semi-metallic or transition metallic elements. Representative examples of preferred elements that are usable in context of the present invention, in an impure form, include, without limitation, magnesium, calcium, aluminum, zinc, sodium, barium, zirconium, manganese, titanium, vanadium, chromium, iron and combinations thereof. The elements are selected according to the desired application of the final hydrophobic composite. For example, hydrophobic powder that includes impure calcium, magnesium and/or zinc bearing a hydrocarbon chain is preferable in cases where the final product is used for building and construction applications.

As used herein, the phrase "hydrocarbon chain" describes a chain of carbon atoms that are covalently attached therebetween and are substituted by hydrogen atoms. The hydrocarbon chain can be linear or branched, saturated or unsaturated chain and therefore can be in he form of alkylene chains that are optionally interrupted

or substituted by, for example, one or more aryl groups. The hydrocarbon chain of the present invention includes at least 10 carbon atoms, preferably at least 12 carbon atoms or more, e.g., 13, 14, 15, 16, 17, 18, 19, 20 or more carbon atoms. Evidently, such a hydrocarbon chain is highly hydrophobic and therefore, when used for coating, renders the powder hydrophobic.

The hydrocarbon chain can be attached to the impure element(s) via various interactions such as electrostatic interactions and Van der Vaals interactions. However, the hydrocarbon chain is preferably covalently attached to the element(s), to thereby form a hydrophobic derivative of the element.

Hence, a preferred hydrocarbon chain according to the present invention is a residue of a hydrophobic organic substance that is capable of reacting with the impure element(s). Such an organic substance has a functional group that can react with the surface of an impure element, the functional group is connected to the hydrocarbon chain.

A representative example of such an organic substance is a fatty acid that has at least 12 carbon atoms. Fatty acids can react with various functional groups that are present on the impure elements' surface via its carboxylic end, to thereby provide the hydrophobic derivative described above. Representative examples of fatty acids that are usable in context of the present invention include, without limitation, stearic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linolenic acid and arachidonic acid.

Hence, the hydrophobic powder of the present invention preferably includes an impure element or a mixture of impure elements, as is defined hereinabove, whereby the selected impurity renders the surface of the element(s) susceptible to chemically reacting with the organic substance described above, which have been reacted with the organic substance to thereby provide the impure element(s) having the hydrocarbon residue of the organic substance covalently attached thereto.

A representative example of a hydrophobic powder that is usable in context of the present invention therefore includes, without limitations, a powder obtained by surface reaction of oxidized element(s) (e.g., colloidal particles of calcium oxide, magnesium oxide and the like), which bear free hydroxyl groups on their surfaces, and a fatty acid such as, for example, stearic acid. The free hydroxyl groups react with the carboxylic group of the fatty acid, so as to form the corresponding ester.

Another representative example of a hydrophobic powder that is usable in context of the present invention include, without limitations, a powder obtained by surface reaction of a carbonated element (e.g., calcium carbonate), which is further impurified with oxidized elements such as magnesium oxide and iron oxide, as well as other substances such as, for example, silicates and sulfates, and a fatty acid as is described hereinabove.

It should be noted, however, that a powder prepared by reacting the surface of calcium carbonate, which have been further impurified, with stearic acid, is commercially available (for example, from Kfar-Gilaadi Quarries, Israel). However, this powder has never been used as a hydrophobic powder and is presently used in the pharmaceutical industry as well as in the plastic industry.

The hydrophobic powder of the present invention is typically characterized by a surface area ranging between 1 m^2/gram and 20 m^2/gram. However, in cases where higher surface area is required, the hydrophobic powder can be grinded so as to enhance the surface area up to more than 50 m^2/gram (e.g., 60 m^2/gram). It should be noted in this respect that the presently known hydrophobic coatings, e.g., the hydrophobic coatings described in U.S. patent No. 4,474,852 and in WO 03/044124, are characterized by surface areas of about 50 m^2/gram.

Due to its particular chemical structure, the hydrophobic powder of the present invention exerts "soap-like" properties and hence it is further characterized as being inactive toward alkaline reagents, such as detergents. Once again it should be noted in this respect that the presently known hydrophobic coatings that are based on hydrophobic colloidal oxides are characterized as being susceptible to such reagents and hence cannot be used in applications that involve the use of detergents.

The hydrophobic powder of the present invention has an average particles size ranging between 0.1 micron and 50 microns, preferably between 0.1 micron and 20 microns, and more preferably between 0.1 micron and 10 microns.

According to a preferred embodiment of the present invention, the hydrophobic powder further comprises hydrophobic fumed silica.

As used herein, the phrase "hydrophobic fumed silica" describes a colloidal form of silica made by combustion of silicon tetrachloride in hydrogen-oxygen furnaces, in which individual particles on the surface thereof have been chemically bonded to hydrophobic trimethoxysiloxyl groups. Hydrophobic fumed silica is a

commercially available powder typically having an average particles size smaller than 1 micron and, if present in the hydrophobic powder of the present invention, it can constitute between 1 and 99 weight percentages of the powder. The resulting mixed powder typically has an average particle size of between 0.1 micron and 20 microns.

Hence, preferred hydrophobic composites according to the present invention include a core material that is coated by a combination of the hydrophobic powder described hereinabove and hydrophobic fumed silica, whereas the partial amount of each of these powders is predetermined either by the selected core material and/or by the intended use of the final product. For example, in applications that require high water repellency, the hydrophobic composite should have smaller particles size and hence the mixed powder should consist a higher amount of the hydrophobic fumed silica. In applications that require lower water-repellency, the hydrophobic composite can have larger particles size and hence the mixed powder consists a higher amount of the hydrophobic powder described hereinabove. The use of a minimal amount of hydrophobic fumed silica is highly advantageous as it substantially reduces the cost of the final product.

In any event, the hydrophobic powder of the present invention, alone or in combination with hydrophobic fumed silica, constitutes between about 0.1 and 5 weight percentages of the hydrophobic composite, whereby powders that include higher amount of the hydrophobic powder described hereinabove constitute between about 2 and about 5 weight percentages of the composite and powders that include higher amount of the hydrophobic fumed silica constitute between about 0.1 and about 2 weight percentages of the composite.

As used herein throughout, the term "about" refers to ± 10 %.

The core material coated by the hydrophobic powder of the present invention may be selected from a wide variety of organic and inorganic substances, with inorganic substances (e.g., minerals) being favored from standpoint of cost and availability.

The physical form of the core material may vary, with particulate and granulate material being preferred. Preferred core materials have an average particles size ranging between about 25 millimeters (25,000 microns) and 5 microns, preferably between 10 millimeters and 20 microns, more preferably between 5 millimeters and 100 microns and most preferably between 1,000 microns and 200 microns. Such a

core material is also referred to herein throughout as aggregate. No-particulated, non-granulated, integral core materials are also within the scope of the present invention.

Representative examples of core materials that are preferably usable in context of the present invention include, without limitation, sand, gravel, slag, porcelanit, dolomite, porcelain, basalt, quartz sand, coal ash, chalk, zeolite, montmorillonite, agapultite, flint, bentonite, perlite, mica, wood chips, nut shells, sawdust and combinations thereof.

A representative example of a preferred core material according to the present invention is quartz sand having a particle size of between 600 and 800 microns.

The hydrophobic composite of the present invention preferably further comprises an adherent layer, which bonds the hydrophobic powder to the core material. The adherent layer serves as a first coat layer deposited on the core material, which anchors the hydrophobic outer coat thereto.

The adherent layer preferably comprises a film forming agent such as a film forming polyurethane. Any of the film-forming polyurethanes commonly employed in the field of coatings may be used in the practice of the present invention. Included in this category are the well-known two-component and one-component polyurethane coating systems. The two-component systems are formed by the reaction of an aliphatic or aromatic isocyanate with a hydroxyl-bearing compound, such as polyfunctional polyesters based on adipic acid, phthalic anhydride, ethylene glycol and trimethylolpropane, for example. Representative of the one-component polyurethane coating systems that may be employed as the adherent layer are those derived from stable isocyanate-terminated prepolymers formed from an aliphatic or aromatic isocyanate and polyfunctional polyether or polyester. These one-component systems are commonly referred to as "moisture cured" polyurethane coatings because drying results from the reaction of the free-isocyanate groups of the pre-polymer with water or atmospheric moisture. Another one-component polymer coating which may be used in the preparation of the hydrophobic composites is the "urethane oil" or "uralkyd", which is the reaction product of a diisocyanate with a hydroxyl-containing drying oil derivative, e.g., that produced by alcoholysis of an unsaturated glyceride with a polyol, such as trimethylolpropane.

The adherent layer of the present invention may further comprise a gluing agent in combination with the film-forming agent, so as to provide an increase in the anchoring quality of the adherent layer over a longer period of time and an increased attraction for oil and oil related products. Hence, the presence and the relative amount of the gluing agent depend on the need of such properties, in accordance with the intended application of the final product.

The gluing agent preferably comprises a volatile hydrocarbon that has at least 12 carbon atoms, such as, for example, asphalt.

As used herein, the term "asphalt" describes a dark brown to black cementitious material in which the predominate constituents are bitumens that occur in nature or are obtained in petroleum processing, the latter being preferred, primarily because of its greater availability. The asphalt may be solid, semi-solid or liquid, with the latter being preferred.

However, other gluing agents, such as, for example, paraffin wax, beeswax, lanolin wax, linseed oil and any other commercially available wax, can be used in this context of the present invention, though their relative amount in the adherent mixture is preferably lower than that of the asphalt.

The adherent layer of the present invention preferably constitutes between about 0.5 and about 7 weight percentages of the hydrophobic composite, more preferably between 1 and 5 weight percentages of the hydrophobic composite, depending on the particles size of the core material, the selected process of preparing the composite and the intended application of the final product. For example, in cases where the core material has an average particles size ranging between 150 microns and 1000 microns, a smaller amount of the adherent layer, e.g. between 0.5 and 1 weight percentage of the hydrophobic composite, is used. In cases where the core material has particles larger than 1000 microns or smaller than 150 microns, a higher amount of the adherent layer is preferred. As is discussed in detail and is further exemplified in the Examples section that follows (see, Examples 5 and 9), using a higher amount of the adherent layer (e.g., more than 1 weight percentage of the composite, preferably 2 weight percentages) results in composites enriched with "free particles", which are characterized by enhanced resistance to dynamic wear. Also, higher amount of adherent layer (e.g., between 3 and 7 weight percentages of the

composite) is required in cases where the hydrophobic composite is prepared in a "cold" process, as is detailed hereinbelow.

As is further described and exemplified in the Examples section that follows (see, Example 10), the required amount of the adherent layer may be predetermined.

The adherent layer of the present invention is easily applied to the core materials by dissolving the film-forming agent and the gluing agent, if present, in a volatile solvent, so as to form a homogeneous composition and to provide a uniform deposition of the adherent layer over the surfaces of the core materials. As is described in detail hereinbelow, such an adherent layer mixture is mixed with the core material while the volatile solvent is evaporated.

Preferred compositions of the adherent layer mixture include a film-forming polyurethane in an amount ranging between 5 and 25 weight percentages of the adherent layer mixture, depending on the size and type of the core material; a gluing agent in an amount ranging between 0 and 25 weight percentages of the adherent layer mixture, depending on the core material used, the gluing agent used and the intended use of the final product; and a volatile solvent in an amount of between 50 and 95 weight percentages of the mixture, depending on the amounts of the other components.

As the volatile solvent merely functions as a vehicle for depositing the adherent layer on the core materials, virtually any volatile solvent in which the components of the adherent layer are soluble may be used. However, preferred solvents include petroleum distillates, such as mineral spirits or paint thinner, which have a boiling temperature of between about 80 °C and about 200 °C. A representative example of a preferred volatile solvent is toluene, which is readily evaporated at relatively low temperatures and results in rapid spread of the mixture onto the core materials.

The hydrophobic composites of the present invention can further comprise various additives which, in accordance with the intended application and the core material used, provide hydrophobic composites with improved characteristics. Representative examples of such additives include, without limitations, coloring agents, UV resistant agents, bleaching agents and abrasive agents.

Coloring agents that are usable in context of the present invention include any of the presently known mineral or organic coloring agents, with mineral coloring

agents being preferred. A preferred amount of the coloring agent added to the composite ranges between about 0.1 and 2 weight percentages of the hydrophobic composite.

The resulting colored hydrophobic composites may be beneficially used in various applications, such as applications that require easy identification of the hydrophobic composite or applications that involve external coating. A representative example of such an application is the use of colored hydrophobic sand to mark submerged cables, so as to warn against excavation nearby. The addition of a coloring agent to the hydrophobic composite is further beneficial as it can sometimes improve the surface tension of the composite, thus rendering it more hydrophobic.

UV resistant agents are added to the hydrophobic composites of the present invention in order to improve the durability of the composites against UV irradiation, and are hence particularly useful in applications such as top-coats of roofs and other surfaces. Representative examples of UV resistant agents that are usable in context of the present invention include, without limitation, titanium dioxide and zinc oxide, both may also serve as bleaching agents. A preferred amount of the UV resistant agent and the beaching agent added to the composite ranges between about 0.01 and 2 weight percentages of the hydrophobic composite.

Abrasive agents are typically added to the hydrophobic composite in order to improve the wear resistance of the composites and are therefore typically used in applications where the composites are exposed to continuous wear. Representative examples of abrasive agents that are usable in context of the present invention include, without limitation, powdered abrasives such as titanium dioxide and aluminium oxide (Al_2O_3, corundum). A preferred amount of the abrasive agent added to the composite ranges between about 0.1 and 0.25 weight percentages of the hydrophobic composite.

The hydrophobic composites of the present invention are therefore comprised of a core material, as is described hereinabove, which is coated by the hydrophobic powder described hereinabove, preferably in combination with hydrophobic fumed silica, and preferably further include an adherent layer, as is described hereinabove. Optionally, the hydrophobic composites of the present invention further comprise additives for improving their properties in accordance with their intended application.

A representative example of a hydrophobic composite according to the present invention is quartz sand coated by a mixture of the hydrophobic powder described

herein and hydrophobic fumed silica, in a ratio that ranges between 20:1 and 2:1, whereby this hydrophobic mixture is bonded to the sand via an adherent layer.

The hydrophobic composites of the present invention are superior to the presently known composites as they include inexpensive and available materials, they are characterized as inactive toward alkaline reagents such as detergents, and, as is demonstrated in the Examples section that follows, they exert superior water-repellency and are further characterized as being capable of preventing water adherence thereto and water penetration therein under an external pressure of at least 3 atmospheres and up to almost 5 atmospheres, and as being highly durable toward dynamic water wear, namely, as remaining hydrophobic under continuous dynamic water wear for at least two months.

The hydrophobic composites of the present invention can therefore be utilized in a myriad of applications, such as, but not limited to, as waterproofing agents in building and pavement construction, as fill or bed materials under concrete slabs or as wall coatings, both below and above ground, as gravel fill or ballast for road beds or sidewalks, as top coats on paved surfaces, in top hole repairs in roadways, as substitutes for common aggregates in asphalt roofing or shingles, or in built-up roofing. In addition, these hydrophobic composites may be applied to painted surfaces to provide a durable, waterproof finish over wood, metal, concrete, stone, brick, and certain synthetic substrates. Additional applications in which the hydrophobic particulates of the present invention may be efficiently used are described in U.S. Provisional Patent Application having the Attorney Docket 03/26316, which is filed concurrently with the instant application and is incorporated by reference as if fully set forth herein.

Further according to the present invention, there is provided a method of preparing the hydrophobic composites described above. In general, the method is effected by coating a core material, as is described hereinabove, with the hydrophobic powder of the present invention, optionally in combination with hydrophobic fumed silica. The amount of the hydrophobic powder and the relative amount of the hydrophobic fumed silica are predetermined as is discussed hereinabove. In cases where a mixture of the hydrophobic powder and the hydrophobic fumed silica is applied, the mixture is prepared is a separate vessel prior to applying thereof to the core material.

In cases where the composite further comprises an adherent layer that bonds the hydrophobic powder to the core material, the method further comprises, prior to coating with the hydrophobic powder, applying onto the core material such an adherent layer, and, more specifically, admixing a pre-prepared adherent layer mixture that contains a film forming agent, a volatile solvent and optionally a gluing agent, as is described hereinabove, with the core material, while removing all of the volatile solvent from the resulting mixture, so as to provide a core material having the adherent layer applied thereon.

As is described in detail in the Examples section that follows, the adherent layer mixture is prepared by mixing its components under heat and is preferably added to the core material while hot. The relative amount of each component in the mixture is predetermined as is discussed hereinabove, while the total amount of the required adherent layer can be also predetermined, as is described and exemplified in the Examples section that follows.

The removal of the volatile solvent is typically performed by evaporative heating, but can alternatively be performed at room temperature.

Hence, the entire process can be performed under heat or alternatively can be performed as a "cold" process, whereas no external heat is applied, as is exemplified in the Examples section that follows. The "cold" process typically involves higher amount of the adherent layer.

In any event, as the core material should contain no more than 1 weight percentage moisture, so as to ensure uniform coatings of the particles, the core material is preferably dried to this extent prior to the coating procedure. The core material is typically dried at a temperature ranging between 90 °C and 120 °C, preferably at about 104 °C. Upon being dried, the core material can be used hot or can be stored in a closed vessel and be thereafter coated while cold.

Once the hydrophobic composite has been prepared, it is preferably cured so as to obtain the final product. The curing time typically ranges between 1 and 30 days, depending on the composition of the hydrophobic powder. For example, in cases where only the hydrophobic powder of the present invention is used, a curing time of 30 days is required. In cases where the hydrophobic powder is in combination with hydrophobic fumed silica, the curing time is shortened proportionally to the relative amount of the hydrophobic fumed silica, and down to 1 day.

Additional objects, advantages, and novel features of the present invention will become apparent to one ordinarily skilled in the art upon examination of the following examples, which are not intended to be limiting. Additionally, each of the various embodiments and aspects of the present invention as delineated hereinabove and as claimed in the claims section below finds experimental support in the following examples.

EXAMPLES

Reference is now made to the following examples, which together with the above descriptions, illustrate the invention in a non limiting fashion.

EXAMPLE 1

PREPARATION OF A HYDROPHOBIC POWDER – GENERAL PROCEDURE

As is described hereinabove, the hydrophobic powder of the present invention includes one or more selected impure elements that have a hydrocarbon attached thereto and optionally hydrophobic fumed silica. The composition of the hydrophobic powder is predetermined according to the desired application.

In cases where the selected hydrophobic powder do not include hydrophobic fumed silica, the hydrophobic powder is preferably prepared by a surface reaction of colloidal particles of one or more selected impure element (e.g., calcium carbonate, magnesium carbonate, calcium oxide, etc.) with a fatty acid having at least 10 carbon atoms in its hydrocarbon chain, to thereby obtain a hydrophobic derivative of the element in a powder form. A representative example of such a hydrophobic powder is Calcium Stearate, which is a commercially available powder that is presently used in pharmaceuticals and plastics. However, such a hydrophobic powder can be prepared, for example, by contaminating calcium carbonate with impurities such as magnesium oxide, iron oxide, aluminium oxide, silica and sulfates, and thereafter reacting the resulting impure calcium with stearic acid.

In cases where the hydrophobic powder further includes hydrophobic fumed silica, the resulting hydrophobic powder mixture is prepared by mixing predetermined amounts of each of the components until uniformity is attained. The mixing is typically continued for about 10 minutes.

A representative example of a hydrophobic powders according to the present invention include a mixture of Calcium Stearate having an average particles size of about 10 microns (obtained from Kfar-Giladi Quarries, Israel) and hydrophobic fumed silica having an average particles size not greater than 1 micron (Earosol Fume Silica, R-812, by Degussa, Germany). The calcium stearate and the fumed silica are mixed for about 10 minutes and the resulting hydrophobic powder has an average particles size not greater than 20 microns.

EXAMPLE 2

PREPARATION OF HYDROPHOBIC COMPOSITES – GENERAL PROCEDURE

Drying the core material: The core material (as is defined hereinabove) is dried at a temperature of at least 104 °C, until its moisture level is reduced to below 1 weight percentage. This procedure is carried out in a closed mixing vessel equipped with a suction port fitted with a valve enabling opening and closure. Alternatively, a pre-dried core material is placed in the mixing vessel described above and is heated to a temperature of at least 70 °C.

Coating the core material with an adherent layer: Preliminary preparation of the adherent layer mixture is carried out in a mixing vessel at a temperature of 40-90 °C, during about 10 minutes (the composition of the mixture is determined as is described hereinabove). The adherent mixture is then added hot as it is into the mixing vessel described hereinabove, which contains the dry core material. The resulting mixture of the dry core material and the adherent layer mixture are thereafter heated and mixed, preferably at 30-60 rpm, such that the solvent is evaporated using the suction system described above. Alternatively, this procedure is carried out without heating, by utilizing the self-heat of the core materials, which is formed during the drying process. This procedure continues until the solvent content reaches 0 % and typically lasts 10-45 minutes, depending on the type of solvent used in the adherent layer mixture. The evaporated solvent is recycled for repeated use, both in order to protect the environment and from an economic standpoint.

In cases where other additives are added to the hydrophobic composite (e.g., coloring agents, abrasive powder, UV resistance agents etc., as is detailed hereinabove), the additive is added to the mixing vessel at this stage and mixing is

continued, preferably at 30-60 rpm, for additional 5 minutes, to obtain uniformity. The added materials should be dried, having moisture content less than 1 %.

Coating the core material coated with the adherent layer with a hydrophobic powder: The hydrophobic powder is prepared as described hereinabove is a separate vessel. The resulting hydrophobic mixture of choice, as is detailed hereinabove, is added into the core material mixture. Upon addition of the hydrophobic mixture, the suction port is closed in order to prevent loss of the hydrophobic material. Mixing is continued for about 10 minutes, until the powder cloud completely disappears. The resulting mixture is then cured for between 24 hours and 30 days, depending on the selected hydrophobic mixture, so as to produce the final hydrophobic composite.

The total time of the process between obtaining the dried core material and obtaining the core material coated by the hydrophobic powder ranges between 25 and 60 minutes.

EXAMPLE 3

PREPARATION OF HYDROPHOBIC COMPOSITES IN A COLD PROCESS – GENERAL PROCEDURE

The core material is dried as is described hereinabove to reach moisture content less than 1 %. The dried core material may be stored in a closed dry place to be used for coating when cold, without any need of re-heating.

An adherent layer mixture, which preferably comprises in this procedure 7 % polyurethane and 93 % ethyl acetate, is prepared as described above and is then added to the dried core material. The quantity of the obtained adherent layer in this process typically ranges between 3 and 7 weight percentages of the dry core material weight. The resulting mixture is mixed at room temperature, for about 10 minutes, until the ethyl acetate is vaporized down to a level of 0 %. The evaporated ethyl acetate may be recycled up to about 80 % of its content.

A hydrophobic coat mixture of choice is then added as is described above and the resulting mixture is mixed for about 5 minutes.

The final product is obtained after curing between 24 hours and 30 days.

EXAMPLE 4

PREPARATION OF HYDROPHOBIC SAND

Sand, such as, for example, quartz sand having particles size of 600-800 microns, was dried as is described hereinabove.

In a separate vessel, an adherent mixture containing 9 weight percentages of the polyurethane Alkydal F 48, 55 % in benzene-xylel (obtained from Bayer, Germany), 5 weight percentages of commercial liquid asphalt (Premier 1430, obtained from Paz-Kar, Israel) and 86 weight percentages of toluene (obtained from Frutarom, Israel) was mixed, at 70 °C, for about 10 minutes and was thereafter added to the hot sand. Mixing was continued for about 15 minutes, at 50 rpm, during which the toluene content was reduced to 0 %.

A hydrophobic powder comprised of between 14:1 and 3:1 Calcium Stearate (obtained from Kfar-Gilaadi Quarries, Israel) and hydrophobic fumed silica (Earosol Fume Silica, R-812, by Degussa, Germany) was prepared in a separate vessel by mixing the components for 10 about minutes and was thereafter added to the hot mixing vessel containing the sand coated by the adherent layer. The suction port was closed and mixing was continued for about 10 minutes at 50 rpm. The product was then cured for 30 days.

EXAMPLE 5

PREPARATION OF HYDROPHOBIC SAND ENHANCED WITH A SURFEIT OF FREE PARTICLES

In a search for hydrophobic sand having improved resistance to dynamic water, it was found that using an increased amount of the adherent layer, (e.g., up to 2 weight percentages of the dry aggregate) as compared with the amount indicated in the presently known procedures for preparing hydrophobic composites (see, for example, U.S. Patent No. 4,474,852), results in enhanced resistance of the hydrophobic sand to dynamic wear, due to addition of small hydrophobic particles to the hydrophobic sand.

This enhanced resistance occurs as a result of the following: when a water wave hits the hydrophobic sand, it pushes the grains somewhat apart and when the wave retreats a momentary under-pressure is created, which pulls out the lightweight granules first. This "migration" of the lightweight particles is only carried out due to

dynamic motion and the particles move towards the dynamic disturbance, so as to form a thin crust of hydrophobic particles forming an additional protection layer. On account of the strong hydrophobic property of the crust, the retreating water does not pull away this crust and the next wave will then encounter a double hydrophobic defense line.

It was found that such lightweight particles may be achieved by using an excessive amount of the adherent layer. In this manner, the adherent layer components, which do not adjoin the sand, form free, light particles having a size of 1-50 microns. These particles become hydrophobic in the second stage, together with the sand granules, and as they are much lighter in weight than the sand granules, they are attracted first to the momentary under-pressure following the wave and thus form the described crust.

A detailed exemplary procedure of preparing such hydrophobic sand, improved with free particles, is as follows:

Quartz sand, obtained from a quarry, having particles size of 600-800 microns, was dried as is described hereinabove.

In a separate vessel, an adherent mixture containing 15 weight percentages of the polyurethane Alkydal F 48, 55 % in benzene-xylel (obtained from Bayer, Germany), 5 weight percentages of commercial liquid asphalt (Premier 1430, obtained from Paz-Kar, Israel) and 80 weight percentages of toluene (obtained from Frutarom, Israel) was mixed, at 70 °C, for about 10 minutes and was thereafter added to the hot sand. Mixing was continued for about 15 minutes, at 50 rpm, during which the toluene content was reduced to 0 %. The amount of the resulting adherent layer deposited on the sand was 2 weight percentages of the dry sand.

A hydrophobic powder comprised of 14:1 Calcium Stearate (obtained from Kfar-Gilaadi Quarries, Israel) and hydrophobic fumed silica (Earosol Fume Silica, R-812, by Degussa, Germany) was prepared in a separate vessel by mixing the components for 10 about minutes and was thereafter added to the hot mixing vessel containing the sand coated by the adherent layer. The suction port was closed and mixing was continued for about 10 minutes at 50 rpm. The product was then cured for 30 days.

EXAMPLE 6

A HYDROPHOBICITY TEST

When hydrophobic sand is serially manufactured, on-going tests of the hydrophobic quality of the finished product are required. The presently known methods measure the contact angle or the surface energy of the produced hydrophobic sand. However, although when properly applied these two methods are accurate and reliable, they require expensive and delicate equipment such as a microscope, a computer and optical equipment and therefore these methods are suited for the laboratory but not for ready and rapid production-line application.

Since the required test is comparative and intended to compare similar production batches in regard to their hydrophobic characteristics, an easy, time-consuming and cost-effective test method is required and has been designed, as follows:

A glass beaker is filled with water up to half its height approximately. A small funnel ("sand glass") is placed above the water surface. The glass beaker is placed on an electronic balance and the balance is zeroed. Hydrophobic sand is then added to the funnel until the sand lump falls into the water. The balance indicates the weight of the hydrophobic sand for comparison.

The underlying principle of this designed test is as follows: Since the sand is hydrophobic, it changes the surface tension of the water so that the sand floats on top of the water. The weight of the hydrophobic sand is practically balanced by the surface tension. Hydrophobic sand attempts to reach the minimum contact area possible with the water so that the sand grains cling to one another and the sand lump directs itself towards the beaker center. The small funnel is constructed such that the streaming of the sand is practically constant and the closeness of the nozzle to the water warrants a practical "floating" of the sand and hardly transfers any kinetic energy which could drop down the sand lump prematurely.

In order to compare various sand samples under identical conditions, as far as possible, the following rules should be observed:

The water must come from the same source, and should preferably be distilled;

The water temperature must be identical in all sample tests;

Testing must begin when the water is in static conditions, preferably in an enclosed space;

All other test data must be identical (beaker, funnel, sand, etc.);

A number of tests must be carried out in parallel, observing the statistical sampling rules.

The test can be carried out automatically by inserting an electric stopper at the funnel nozzle, and a detector that indicates the exact moment when the sand lump falls and then halts the sand flow by means of a shutdown valve.

EXAMPLE 7
CORROSIVITY TEST

In order to verify the protection capability of the hydrophobic sand of the present invention against corrosion of iron, the following corrosivity test has been performed:

Into a container filled with sea-sand, three standard polygonal reinforcing iron construction bars of 10 mm diameter were inserted. The three bars were of identical length and weight. The first bar was dressed with concrete throughout its length in a diameter of about 10 cm, apart from the tip of the bar, which was left exposed for electric connection. Based on the assumption that corrosion level within cast and impacted concrete would be minimal, this bar was intended to serve as control against the two other bars and is referred to hereinafter as control bar. The second bar was left in its natural state and sunk into the sea sand as is, apart from its tip which was left exposed for electric connection, and is referred to hereinafter as natural bar. The third bar was sunk in sea sand surrounded throughout its length with the hydrophobic sand of the present invention (prepared as described in Example 4) in a diameter of about 10 cm, apart from the its tip which was left exposed for electric connection, and is referred to hereinafter as hydrophobic bar.

The second (natural) and third (hydrophobic) bars were electrically connected to the concrete-encrusted bar (control) through 100 ohm resistors.

The sea sand was wetted with water including 8 % sodium chloride, added in order to accelerate the corrosion process. The sand wetting was carried out once in a fortnight in order to allow natural drying-up by evaporation.

The electric potentials between the second natural bar (natural) and the control, as well as between the third bar (hydrophobic) and the control bar, were measured every day. The presently obtained data show that the potential difference between the natural bar and the control bar stabilized at a fixed level (about 100 millivolt) thus confirming an on-going corrosion process in the natural bar, whereas the potential difference between the hydrophobic bar and the control bar remained throughout at zero level, confirming that no corrosion was taking place and that the sand indeed protects the iron bar against corrosion.

The test is currently ongoing, with the intention to pull out the bars from the sea sand after six months. Then, the iron bars will be re-weighed, in order to factually determine the corrosion level of the natural and hydrophobic bars and to bear out the electrical measurement.

In order to obtain interim data prior to the above laboratory test, uncoated metal paper clips were inserted into a box containing on one-half ordinary sand and on the other half the hydrophobic sand of the present invention, such that one-half of the clips were immersed in the ordinary sand and the other half in the hydrophobic sand of the present invention (prepared as described in Example 4). The experiment was carried out with 10 identical boxes of such clips.

In an additional experiment, 10 pairs of ordinary AAA batteries were submerged in garden soil, whereby one battery of each pair was submerged in the hydrophobic sand of the present invention.

The paper clip boxes were wetted with salt water for about two weeks, whereas the battery pairs were left buried for about two months in the change of seasons between winter and spring, so that the soil was wetted both with rainwater and with artificial irrigation, as is the rule for ordinary garden soil.

After two weeks all the paper-clip boxes opened showed an identical result of corrosion and rust in the half of the paper clip buried in the ordinary sand whereas the other half of the paper clip boxes, buried in the hydrophobic sand of the present invention remained intact without signs of corrosion.

All the batteries buried in regular garden earth showed signs of corrosion at various levels and no electric voltage was measured in these batteries, whereas no sign of corrosion was observed in any battery buried in the hydrophobic sand of the present invention and the voltage in those batteries was indeed preserved.

EXAMPLE 8

WEAR TEST

Most of the presently known sealants are usually tested to withstand static water, i.e., water devoid of kinetic energy. At this situation, sealant wear occurs as a result of the reaction between the water and the material, liquid adsorption, expansion or contraction and as a result of the proliferation of various organisms in the standing water, which also accelerates the wear process of the sealant.

However, under real conditions, the sealant must also stand up against dynamic water, since in most cases water do possess kinetic energy. In every case of wetting, natural or artificial, one can see a vertical or horizontal water motion resembling a wave. Just as a sea wave that slams onto the beach and causes a breakup of soil and erosion together with its retreat, in wetting, the water wave accelerates the wear of the sealant and such wear is much faster than the wear caused by static water.

Most of the water motion wear is caused in nature due to solids transported with the water such as sand, various aggregates etc.. Therefore, in order to simulate natural wear, a wearing material such as iron oxide powder (Fe_2O_3) should be added to the water.

Hence, due to lack of data regarding the effect of real water wear, comparative tests have been conducted, in order to determined the lifetime of the hydrophobic sands of the present invention, compared with other known sealants, and the required thickness of the hydrophobic sands of the present invention.

Hence, two sets of tests were carried out: In the first set tests have been conducted in order to compare between layers of polystyrene, PVC, bituminous sheet, the hydrophobic sand of the present invention (see, Example 4) and the hydrophobic sand improved with free particles of the present invention (see, Example 5). In the second set, five samples of the hydrophobic sand improved with free particles of the present invention (Example 5) having varying thickness between 1 cm and 5 cm were tested for their water wear.

The tests were carried out as follows: A transparent glass beaker equipped with a screw-down metal lid was provided. Into the metal lid a layer of sponge on which the tested sealant was laid was inserted, so that the sample extended over the edge of the glass beaker. Water including 10 % iron powder was admitted to the beaker so as to fill one quarter of its area. The lid was screwed down on top of the

beaker with the sealant sample serving as gasket. The closed beaker was placed inverted, with the lid down, so that the water covered the sample.

Five beakers, each comprising a different sealant or the same sealant having varying thickness, were placed together on a rotary turntable driven at a fixed speed of 45 rpm. Since these tests were comparative, the beakers were driven together, the water thereby performing a relative circumferential motion around each beaker. Beakers are taken down when the water penetrate the sealant surface and reach the downwards pressing sponge. The total rotation time of each beaker is noted down, considering that one water rotation in the glass simulates one wetting cycle or a single wave. Since the PVC sheet wear lifetime is known, a coefficient is determined for the number of wettings per day so that the test time can be compared based on sealant lifetime in months.

The tests described above are still ongoing and hence no final data have been obtained heretofore. However, interim data indicate that the beaker containing polystyrene was taken down after 4 days and further indicate that during the present course of the experiment (about two months) no water has been penetrated the sealant surface in the beakers containing the hydrophobic sands of the present invention.

EXAMPLE 9

DURABILITY OF HYDROPHOBIC COMPOSITES UNDER EXTERNAL PRESSURE

The capability of hydrophobic aggregates to withstand water pressure is proportional to the contact angle cosine and is inversely proportional to the capillary radius or the inter-granule clearance radius. Hence, in order to obtain a hydrophobic aggregate that is capable of withstanding high water pressure without being cracked or loosing its hydrophobicity, an aggregate having small particle size (such that the inter-granule clearance radius is minimal) coated by a hydrophobic layer with high contact angle should be used.

In order to measure the capability of hydrophobic aggregates to withstand transitory and continuous pressure, the following test has been designed:

A wide and deep pail is perforated at its bottom with holes that are covered with a porous cloth, passing water but not sand. The pail is filled with hydrophobic sand.

The nozzle of a long syringe is cut off, so as to provide a uniform cylinder. The syringe cross-sectional area is chosen to be 1 cm^2, for convenience. Rubber bands are stretched on the syringe external surface, so as to roughen it, and the external surface of the syringe is further covered by a bitomenic paste (or any other gluing agent that is not water-based), so as to attach hydrophobic sand thereto and thereby prevent water passage from the syringe into the hydrophobic sand.

The syringe is inserted into the hydrophobic sand in the pail, so as to make the distance from the cut-off nozzle to the pail bottom serve as the thickness of the tested layer. The syringe is anchored to the pail walls on two sides, such that the syringe distance from any wall is larger than the thickness of the tested layer, to prevent water from "taking the shorter path".

The piston handle top is widened to enable it to take weights, and the thus modified piston is accurately weighed.

The syringe is then half-filled with water and the piston is carefully inserted thereto.

By placing weights on the piston top it is possible to measure the pressure in the long run, as well as to establish the burst-out pressure.

Such a test allows performing comparative tests of the capability to withstand water pressure of various hydrophobic aggregates, assuming the aggregate is incompressible. This assumption must be carefully verified for each type of hydrophobic aggregate tested.

As a representative example, the test described above was performed with a hydrophobic sand prepared as described hereinabove, having a particles size of between 300 and 600 microns and a hydrophobic powder that forms with water a contact angle of 130 °C.

A weight of 3 kg (including the piston self-weight) was placed on the piston for 48 hours. The water head remained unchanged during this time period. The load was thereafter gradually increased until burst-out occurred at 4.6 kg.

EXAMPLE 10

DETERMINATION OF THE ADHERENT LAYER AMOUNT

The core materials that are usable in the hydrophobic composites of the present invention are granulated or particulate materials each characterized by a

different shape, surface area, absorbency, surface texture and various other mechanical and chemical characteristics. Therefore, different core materials absorb different quantities of the adherent layer of the present invention until they becomes fully coated.

It is therefore desirable to calculate the quantity of the adherent layer required to coat a specific core material, both from an economic standpoint and in order to produce hydrophobic composites improved by "free particles", which require excessive amount of the adherent layer, as is detailed hereinabove (see, Example 5).

In order to determine the amount of an adherent layer that is required to fully coat a certain core material, the following test has been designed:

First, the tested core material is sieved to remove small particles. Measured samples of the remaining material are thereafter accurately weighed. The core material is then coated by an adherent layer and a hydrophobic powder, as is described hereinabove, whereby the amount of the adherent layer is much higher than in typical procedures and the amount of the hydrophobic powder is standard and is accurately weighed. As is described hereinabove (in Example 5), such high amounts of the adherent layer result in hydrophobic sand having a surfeit of free particles.

The resulting hydrophobic composite is then cured and is thereafter passed again through the same sieve as before to remove the free particles formed. Measured volumes of samples of the sieved hydrophobic composites are accurately weighed. The weight of the hydrophobic powder added is subtracted from the weight of the hydrophobic composite and the resulting weight is divided by the initial weight of the sample. The obtained ratio expresses the relative amount of the adherent layer in the composite.

Following is a representative example of the described test:

Common building sand was sieved through a 200 micron mesh sieve to remove small particles. Three samples, 500 cm^3 each, were weighed, yielding the following results: Sample 1 = 812 grams; Sample 2 = 836 grams; Sample 3 = 821 grams; Mean weight = 823 grams.

The sieved sand was thereafter coated by 20 grams of adherent layer and 1.5 grams of hydrophobic powder per each 823 gram quantity of the mixture.

After curing, the sand was re-sieved using the same sieve as before to remove free particles.

Again, three samples of the hydrophobic sand were weighed, yielding the following results: Sample 1 = 818 grams; Sample 2 = 839.3 grams; Sample 3 = 832.1 grams; Mean weight = 829.8 grams.

Subtraction of the hydrophobic powder amount (1.5), a ratio of (829.8 – 1.5)/823 = 0.64 % was obtained, expressing the amount of adherent layer deposited on the core material in the process.

It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable subcombination.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims. All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

WHAT IS CLAIMED IS:

1. A hydrophobic composite comprising a core material coated by a hydrophobic powder, said hydrophobic powder comprises at least one impure element having a hydrocarbon chain attached thereto.

2. The hydrophobic composite of claim 1, wherein said hydrocarbon chain comprises at least 10 carbon atoms.

3. The hydrophobic composite of claim 1, wherein said hydrocarbon chain is covalently attached to said at least one impure element.

4. The hydrophobic composite of claim 3, wherein said hydrocarbon is a residue of a fatty acid having at least 12 carbon atoms.

5. The hydrophobic composite of claim 4, wherein said fatty acid is selected from the group consisting of stearic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linolenic acid and arachidonic acid.

6. The hydrophobic composite of claim 1, wherein said element is selected from the group consisting of a metallic element, a semi-metallic element and a transition metallic element.

7. The hydrophobic composite of claim 1, wherein said at least one element is selected from the group consisting of magnesium, calcium, aluminum, zinc, sodium, barium, zirconium, manganese, titanium, vanadium, chromium, iron and combinations thereof.

8. The hydrophobic composite of claim 1, wherein said hydrophobic powder has an average particle size ranging between 0.1 micron and 50 microns.

9. The hydrophobic composite of claim 1, wherein said hydrophobic powder has a surface area ranging between 1 m^2/gram and 60 m^2/gram.

10. The hydrophobic composite of claim 1, characterized as being inactive toward alkaline reagents.

11. The hydrophobic composite of claim 1, being capable of preventing water adherence thereto and water penetration therein under an external pressure of up to about 4.5 atmospheres.

12. The hydrophobic composite of claim 1, characterized by being durable to dynamic water wear for at least 2 months.

13. The hydrophobic composite of claim 1, wherein said hydrophobic powder is bonded to said core material via an adherent layer.

14. The hydrophobic composite of claim 1, wherein said core material is selected from the group consisting of a particulate material and a granulate material.

15. The hydrophobic composite of claim 1, wherein said core material is selected from the group consisting of sand, gravel, slag, porcelanit, dolomite, porcelain, basalt, quartz sand, coal ash, chalk, zeolite, montmorillonite, agapultite, flint, bentonite, perlite, mica, wood chips, nut shells, sawdust and combinations thereof.

16. The hydrophobic composite of claim 14, wherein said core material has an average particle size ranging between 25 millimeters and 5 microns.

17. The hydrophobic composite of claim 15, wherein said core material is quartz sand.

18. The hydrophobic composite of claim 13, wherein said adherent layer comprises a film-forming agent.

19. The hydrophobic composite of claim 18, wherein said film forming agent is a film forming polyurethane.

20. The hydrophobic composite of claim 18, wherein said adherent layer further comprises a gluing agent.

21. The hydrophobic composite of claim 18, wherein said gluing agent is a volatile hydrocarbon having at least 12 carbon atoms.

22. The hydrophobic composite of claim 21, wherein said gluing agent is selected from the group consisting of liquid asphalt, paraffin wax, beeswax, lanolin wax, linseed oil and combinations thereof.

23. The hydrophobic composite of claim 20, wherein said gluing agent constitutes between about 0.1 and about 50 weight percentages of said adherent layer.

24. The hydrophobic composite of claim 1, wherein said hydrophobic powder further comprises hydrophobic fumed silica.

25. The hydrophobic composite of claim 24, wherein said hydrophobic fumed silica constitutes between 1 and 99 weight percentages of said hydrophobic powder.

26. The hydrophobic composite of claim 13, wherein said adherent layer constitutes between about 0.5 and about 7 weight percentages of the hydrophobic composite.

27. The hydrophobic composite of claim 1, wherein said hydrophobic powder constitutes between about 0.1 and about 5 weight percentages of the hydrophobic composite.

28. The hydrophobic composite of claim 24, wherein said hydrophobic powder constitutes between about 0.1 and about 5 weight percentages of the hydrophobic composite.

29. The hydrophobic composite of claim 1, further comprising at least one additive selected from the group consisting of a coloring agent, a UV resistant agent, a bleaching agent and an abrasive agent.

30. The hydrophobic composite of claim 29, wherein said coloring agent constitutes between about 0.1 and about 2 weight percentages of the hydrophobic composite.

31. The hydrophobic composite of claim 29, wherein said UV resistant agent and said bleaching agent each constitutes between about 0.01 and about 2 weight percentages of the hydrophobic composite.

32. The hydrophobic composite of claim 29, wherein said abrasive agent constitutes between about 0.1 and about 0.5 weight percentages of the hydrophobic composite.

33. A method of preparing a hydrophobic composite, the method comprising coating a core material with a hydrophobic powder, said hydrophobic powder comprises at least one impure element having a hydrocarbon chain attached thereto, to thereby provide the hydrophobic composite.

34. The method of claim 33, further comprising, prior to said coating, applying onto said core material an adherent layer, said adherent layer bonding said hydrophobic powder to said core material.

35. The method of claim 34, wherein said step of applying onto said core material an adherent layer comprises admixing said core material with an adherent mixture containing a film-forming agent and a volatile solvent, while removing all of said volatile solvent from the mixture of said core material and said adherent mixture, to thereby provide said core material having applied thereon said adherent layer.

36. The method of claim 33, further comprising drying said core material prior to said coating.

37. The method of claim 35, further comprising drying said core material prior to said admixing.

38. The method of claim 33, further comprising, after said coating, curing said hydrophobic composite.

39. The method of claim 38, wherein said curing is performed for a time period ranging between 1 and 30 days.

40. The method of claim 35, wherein said removing of said volatile solvent is performed by evaporative heating.

41. The method of claim 35, wherein said removing of said volatile solvent is performed at room temperature.

42. The method of claim 35, wherein said volatile solvent is an organic solvent having a boiling temperature ranging between about 80 °C and 200 °C.

43. The method of claim 33, further comprising, prior to said coating, admixing said core material with an additive selected from the group consisting of a coloring agent, a UV resistant agent, a bleaching agent and an abrasive agent.

44. The method of claim 35, further comprising, prior to said coating, admixing said core material having thereon said adherent layer with an additive selected from the group consisting of a coloring agent, a UV resistant agent, a bleaching agent and an abrasive agent.

45. The method of claim 33, wherein said core material is selected from the group consisting of a particulate material and a granulate material.

46. The method of claim 45, wherein said core material is selected from the group consisting of sand, gravel, slag, porcelanit, dolomite, porcelain, basalt, quartz

sand, coal ash, chalk, zeolite, montmorillonite, agapultite, flint, bentonite, perlite, mica, wood chips, nut shells, sawdust and combinations thereof.

47. The method of claim 45, wherein said core material has an average particle size ranging between 25 millimeters and 5 microns.

48. The method of claim 46, wherein said core material is quartz sand.

49. The method of claim 35, wherein said film forming agent is a film forming polyurethane.

50. The method of claim 35, wherein said adherent mixture further comprises a gluing agent.

51. The method of claim 50, wherein said gluing agent is a volatile hydrocarbon having at least 12 carbon atoms.

52. The method of claim 51, wherein said gluing agent is selected from the group consisting of liquid asphalt, paraffin wax, beeswax, lanolin wax, linseed oil and combinations thereof.

53. The method of claim 33, wherein said hydrophobic powder has an average particle size ranging between 0.1 micron and 50 microns.

54. The method of claim 33, wherein said hydrophobic powder has a surface area ranging between 1 m^2/gram and 60 m^2/gram.

55. The method of claim 33, wherein said hydrophobic powder further comprises hydrophobic fumed silica.

56. The method of claim 55, wherein said hydrophobic fumed silica constitutes between 1 and 99 weight percentages of said hydrophobic powder.

57. The method of claim 35, wherein said adherent layer constitutes between about 0.5 and about 7 weight percentages of said hydrophobic composite.

58. The method of claim 33, wherein said hydrophobic powder constitutes between about 0.1 and about 5 weight percentages of said hydrophobic composite.

ABSTRACT OF THE DISCLOSURE

Novel hydrophobic composites that exert improved water-repellency and durability are disclosed. The hydrophobic composites are prepared by coating a core material with a hydrophobic powder which comprises hydrophobic derivatives of impure elements.